perimental support to the postulate of orbital stabilization.[4] The susceptibility of the *mono* compound, 1.8 B.M., corresponds to one unpaired electron. This is not consistent with the theoretical values expected from the simple formula [Fedipy-Cl_2] and may suggest a certain amount of metal-metal interaction. Detailed studies on these and similar compounds will be published later.

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THE OXYGEN-HYDROGEN PEROXIDE COUPLE AT THE DROPPING MERCURY ELECTRODE

Sir:

The first oxygen wave of the dropping mercury electrode (D.M.E.) arises from the two electron reduction of oxygen to hydrogen peroxide. Although this wave has universally been considered highly irreversible,[1] it was recently reported[2] that in unbuffered basic solutions hydrogen peroxide yields an anodic wave at the same potential. From this and other observations the investigators concluded that the oxygen–hydrogen peroxide reaction is completely reversible, but involves only one electron.

These conclusions are not consonant with the fact that H_2O_2 (or HO_2^-) and O_2 must be the diffusing species, and hence two electrons be involved in the over-all electrode process; and they conflict with the insensitivity of the oxygen half-wave potential ($E_{1/2}$) to changes in *p*H, as reported by Kolthoff and Miller.[3] In view of the fundamental importance of the oxygen wave in polarography, it was considered important to resolve this problem, and a preliminary report is provided in this Communication.

Polarograms of oxygen, hydrogen peroxide and their mixtures were run in buffered solutions, *p*H range 7.5–13, of ionic strength 0.15. In all these solutions, anodic and cathodic waves were observed, which in the less basic media exhibited the usual criteria of irreversibility—drawn-out shapes, non-linear "log plots," and in the case of the oxygen wave an $E_{1/2}$ which hardly varied with *p*H. In mixtures of hydrogen peroxide and oxygen the two waves joined without inflection; however, the $E_{1/2}$ shifted as the composition of the mixture was varied. This irreversible nature diminished as the alkalinity increased, until at *p*H 12 both anodic and cathodic waves gave identical $E_{1/2}$'s, and the log plot of both had the theoretical slope for a two-electron reaction.

At the point at which the electrolysis current in a H_2O_2–O_2 mixture crosses the residual current, the D.M.E. is functioning as a potentiometric null point detector. The "crossing point" potential will depend upon the bulk concentration as predicted by the Nernst equation, provided that we are dealing with the over-all reaction

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad (1)$$

for which the Nernst equation at 25° is

$$E = E^0 + 0.0296 \log (O_3)/(H_2O_2) - 0.0592\, pH \qquad (2)$$

Supposing that the absolute rate theory as recently applied to polarographic phenomena[4] is applicable here, it can be shown that these equations apply at the crossing point, however irreversible the waves may be.

In fact, Equation (2) was found to hold very well both with regard to the *p*H and the O_2–H_2O_2 ratio (corrected for the acid dissociation of H_2O_2) over the entire range investigated. The value $E^0 = +0.70$ v. ± 0.01 v. was found for the standard potential of the half-cell of Equation (1), in good agreement with Latimer's calculated value +0.682 v.[5]

These experimental results are also in good accord with the observations of Berl,[6] who found that the O_2–H_2O_2 couple was reversible at graphite and activated carbon electrodes in solutions of *p*H between 13 and 15, with an E^0 of +0.684 v.

In the range of *p*H studied the O_2–H_2O_2 couple at the D.M.E. evidently is of the transition (semi-reversible) type.[7] The situation is complicated by the probable presence of two steps[8] which may differ in degree of reversibility and dependence on *p*H. Analysis of the irreversible nature of the waves is continuing with the hope of elucidating the mechanism and kinetics of oxygen reduction. The combined results will be presented in a future publication.

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(1) Kolthoff and Lingane, "Polarography," 2nd edition, Vol. II, Interscience Publishers, Inc., New York, N. Y., p. 552.

(2) S. Hacobian, *Australian Journal of Chemistry*, **6**, 211 (1953).

(3) I. M. Kolthoff and C. S. Miller, THIS JOURNAL, **63**, 1013 (1941).

(4) Tanford and Wawzonek, "Annual Reviews of Physical Chemistry," **3**, 247 (1952).

(5) W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., p. 43.

(6) W. G. Berl, *J. Electrochem. Soc.*, **83**, 253 (1943).

(7) P. Delahay, THIS JOURNAL, **75**, 1430 (1953); M. Smutek, *Coll. Czech. Chem. Comm.*, **18**, 171 (1953).

(8) One of these may be the reversible one-electron step postulated by Hacobian, see ref. 2.

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9α-FLUORO DERIVATIVES OF CORTISONE AND HYDROCORTISONE

Sir:

In a recent communication[1] we have described a new group of derivatives of cortisone and hydrocortisone, in which the 9α-hydrogen atom is replaced by halogen. The main interest in this series of compounds derived from the fact that they possessed marked glucocorticoid activity, which in the case of the chloro derivatives exceeded by a factor of 4 that of the parent hormones. The finding that the activity was inversely proportional to the size of the halogen atom prompted the preparation of the last remaining members of this group, the 9α-fluoro derivatives, the description of which is the purpose of this communication.

9α-Fluorohydrocortisone acetate (I), m.p. 233–234°[2]; $[\alpha]^{23}D$ +123° (*c*, 0.64 in $CHCl_3$); $\lambda_{max.}^{alc.}$ 238 mμ (ε = 16,800); $\lambda_{max.}^{Nujol}$ 2.94 μ, 3.03 μ (OH), 5.75 μ, 5.82 μ (acetylated side chain), 6.07 μ, 6.11 μ

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(1) J. Fried and E. F. Sabo, THIS JOURNAL, **75**, 2273 (1953).

(2) Occasionally samples began to melt at 205–208°, resolidified and eventually melted at 226–228°, probably due to polymorphism.